Introduction to the BAC methods

The thermodynamic and other molecular properties found in this database are all obtained from Bond Additivity Correction (BAC) calculations, a class of quantum-chemistry based methods developed by C.F. Melius, in collaboration with P. Ho and M.D. Allendorf, and described in detail in various publications.[1-4] The BAC methods are based on the assumption that errors in electronic energies obtained from *ab initio* calculations are due to the finite size of the basis sets used and the application of limited electron correlation in the calculations. These errors are therefore systematic and can be corrected to achieve much greater accuracy for predicted heats of formation by applying a variety of empirical corrections related to the elements and bonds in the molecule.

The BAC suite of methods currently comprises several levels of theory. The most widely applied is the BAC-MP4 method, which was developed first. In this method, the molecular electronic energy is obtained from an *ab initio* electronic-structure calculation at the level of fourth-order Moller-Plesset perturbation theory. Methods using second-order Moller-Plesset perturbation theory (BAC-MP2), G2 theory (BAC-G2), and a hybrid method involving both density functional theory and MP2 have also been developed; these use a different approach for determining the empirical corrections to the *ab initio* electronic energy than the original BAC-MP4 method.

The BAC-MP4 method

The BAC-MP4 method is shown schematically in Figure 1; the individual calculations are described below. All calculations were performed using the Gaussian suite of quantum-chemistry codes;[5] the precise version of the code used for a particular MP4 calculation is given in the database in most cases.

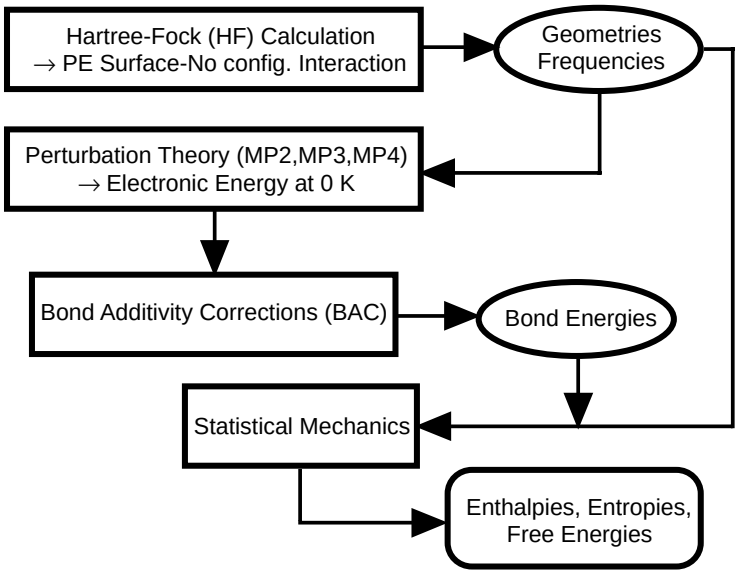

Figure 1. Schematic of the BAC Method

Molecular geometries, vibrational frequencies, and moments of inertia. The molecular equilibrium geometry is required input for the MP4 calculation used in the BAC-MP4 method. This geometry and the frequencies and moments of inertia derived from it are also used in post-*ab initio* calculations to obtain thermodynamic data at temperatures above 0 K.

In the BAC-MP4 method, equilibrium geometries and harmonic vibrational frequencies are obtained from Hartree-Fock (self-consistent field) theory (an introduction to these and other quantum-chemistry methods can be found in Ref. 6). Restricted Hartree-Fock theory (RHF) is used for closed shell molecules and unrestricted Hartree-Fock theory (UHF) is used for open-shell molecules, using the 6-31G(d) basis set. Vibrational frequencies calculated at this level of theory are known to be systematically larger than experimental values; thus, each calculated frequency is scaled by dividing it by 1.12.[7]

Electronic energies. To determine atomization enthalpies and thus heats of formation, the effects of electron correlation are included by performing single-point calculations, using Moller-Plesset perturbation theory (MP4 using the 6-31G(d,p) basis set with single, double, triple and quadruple substitutions) and the HF/6-31G(d) geometries.

Bond additivity corrections and corrected heats of formation. The form of the BAC parameters α_{ij}, A_{ij}, and B_k used to calculate the corrections for individual molecules is given in Equations 1-4, using the example of a bond between atoms X_i and X_j in a molecule of the form X_k-X_i-X_j :

$$E_{\mathrm{BAC}}(X_i\text{-}X_j) = f_{ij} g_{kij} \quad (1)$$

where

$$f_{ij} = A_{ij} \exp(-\alpha_{ij} R_{ij}) \quad (2)$$

$$g_{kij} = (1. - h_{ik} h_{ij}) \quad (3)$$

$$h_{ik} = B_k \exp\{-\alpha_{ik}(R_{ik} - 1.4\ \text{Å})\} \quad (4)$$

A_{ij} and α_{ij} are empirically derived parameters that depend on the X_i-X_j bond type and R_{ij} is the bond distance (Ångstroms). The factor B_k in Equation 4 is used to derive a correction for the effects of neighboring atoms on the X_i-X_j bond (Equation 3) and depends on the identity of atom *k*.

A correction is also made in the case of open-shell molecules for spin contamination of the ground state by excited electronic states. The error in the electronic energy caused by this effect was estimated using the approach of Schlegel[8] and is given by

$$E_{\mathrm{BAC}}(\text{spin } S^2) = E(\text{UMP3}) - E(\text{PUMP3}) \quad (5)$$

where E(UMP3) is the third-order MP energy using the UHF wavefunction and E(PUMP3) is the projected UMP3 energy. This correction is generally small (~ 0.5 kcal mol^{-1}) but may become large for molecules containing a high degree of unsaturation or low-lying electronic excited states. Closed-shell molecules that are UHF-unstable, such as SiH_2, also require an additional correction. The form of the correction is:

$$E_{\mathrm{BAC}}(\mathrm{spin}_{\mathrm{UHF\text{-}unstable}}) = K_{\mathrm{UHF\text{-}I}} S(S+1) \qquad (6)$$

where $K_{\mathrm{UHF\text{-}I}}$ is 10.0 kcal mol^{-1} (based on the heat of formation of O_3) and S is the spin obtained from the UHF/6-31G(d,p) calculation. Application of this correction yields reasonable heats of formation for singlet SiH_2 and CH_2.

Table 1 lists the parameters A_{ij}, α_{ij} and B_k used in this work for each bond type, all of which were determined previously. References are also given where detailed information can be found concerning the basis used for establishing these values.

Table 1. BAC Parameters for the BAC-MP4 (SDTQ) Level of Theory.

Bond	**A_{ij} (MP4)[a]**	**α_{ij}(MP4)[b]**	**Reference**
H-H	18.98	2.000	3
B-H	31.12	2.000	9
B-B	969.88	3.800	10
B-N	370.10	2.840	9
B-F	206.89	2.650	11
B-Si	45.77	1.000	10
B-Cl	172.49	2.000	9
C-H	38.61	2.000	11
C-C	1444.09	3.800	11
C-N	462.33	2.800	11
C-O	175.62	2.141	11
C-F	143.29	2.100	11
C-Cl	304.26	2.000	11
N-H	70.08	2.000	11
N-N	472.62	2.600	11
N-O	226.04	2.100	11
O-H	72.45	2.000	11
O-O	169.78	2.000	11
Si-H	92.79	2.000	1,12
Si-C	893.71	2.500	13
Si-N	847.99	2.500	14
Si-O	7038.50	3.978	15
Si-F	260.65	2.000	2
Si-Si	3330.21	2.700	12
Si-Cl	721.93	2.000	1
Cl-H	116.40	2.000	11
Cl-O	355.14	2.000	11
Cl-Cl	980.18	2.000	11
F-H	84.21	2.000	11
F-N	170.05	2.000	11
F-O	189.70	2.000	11
F-F	129.17	2.000	11
Atom	**B_k(MP4)**		
H	0.0		

B	0.200		
C	0.310		
N	0.200		
O	0.225		
F	0.330		
Si	0.2		
Cl	0.42		

[a] in kcal mol^{-1}
[b] in Å^{-1}

Table 2. Atomic heats of formation (0 K), kcal mol^{-1}, used to calculate heats of formation.

Atom	ΔH_{f0}^{o}	**Reference**
H	51.63	16
B	133.8	17
C	169.98	16
O	58.99	16
N	112.53	16
F	18.48	16
Si	106.66	16
Cl	28.59	16

Atomization energies and heats of formation at 0 K. The sum of the BACs is combined with the MP4(SDTQ) electronic energy and the unscaled zero-point energy to obtain the heats of atomization and formation at 0 K (ΣD_O and $\Delta H°_f$ (0 K), respectively). Values of the atomic heats of formation used in this calculation are given in Table 2.

The corrected $\Delta H°_f$ (0 K) is obtained as follows. First, the calculated molecular electronic energy is added to the zero-point energy (calculated from the unscaled vibrational frequencies). Next, the resulting energy is subtracted from the calculated electronic energies of the atoms to give an electronic heat of atomization:

$$E_{\text{atomization}} = \sum_{i}^{n} E_i(\text{atoms}) - (E_{\text{ab initio}}(\text{molecule}) + E_{\text{ZPE}}) \quad (7)$$

Referencing this energy against the experimental $\Delta H°_f$ (0 K) of the atoms in the gas phase (Table 2) yields the uncorrected molecular $\Delta H°_f$ (0 K):

$$\Delta H^{\circ}_{\text{f0, uncorrected}} = \sum_{\text{atoms}} \Delta H^{\circ}_{\text{f0, atoms}} - E_{\text{atomization}} \quad (8)$$

Subtracting the BAC corrections from this energy finally yields the corrected (BAC-MP4) $\Delta H°_f$ (0 K):

$$\Delta H^{\circ}_{f0,BAC} = \Delta H^{\circ}_{f0,uncorrected} - E_{BAC\text{-}Correction} \quad (9)$$

Thermodynamic data as a function of temperature. Entropies, heat capacities, enthalpies, and free energies as a function of temperature are calculated using the heats of formation at 0 K, moments of inertia, and vibrational frequencies. Equations derived from statistical-mechanics, an extension of the subroutines in the Gaussian codes, are employed.[5] These subroutines use standard expressions for an ideal gas in the canonical ensemble to compute the heat capacity, enthalpy, and entropy. For consistency with previous work, unscaled frequencies are used to determine ΔH°_f (0 K), while the scaled frequencies are used to calculate thermochemistry at higher temperatures. Minor differences that would result from using the scaled frequencies to calculate ΔH°_f (0 K) are incorporated into the BACs.

Treatment of Hindered Rotors. Contributions to the heat capacity and entropy from rotating groups are accounted for by substituting a hindered rotor for the corresponding vibrational frequency determined by the HF calculation. Approximate analytical functions have been developed to estimate the hindered rotor energy E_{hr}, heat capacity C_{hr}, and entropy change ΔS_{hr}.[18] The expressions are

$$E_{hr} = RT (1/2 + Y - g(Y)) (x / (e^x - 1)) \quad (10)$$

$$C_{hr} = R (1/2 + Y^2 - g(Y) - g(Y)^2) (x^2 / (e^x - 1)^2) \quad (11)$$

$$\Delta S_{hr} = R (\ln(SI_0) + Y - g(Y)) (z^2 e^z / (e^z - 1)^2) \quad (12)$$

where

$$g(Y) = Y (SI_1 / SI_0) \quad (13)$$

$$Y = V / 2RT \quad (14)$$

$$x = (1.67 / I_r) \text{ sqrt } (V / RT) \quad (15)$$

and

$$z = 3.8 / I_r \quad (16)$$

where $SI_m(Y)$ is the scaled modified Bessel function of order m. The expressions in eqns. 10 - 12 are exact for $I_r \rightarrow \infty$, as derived by Pitzer and Gwinn.[18] Eqns. 10 - 12 do an excellent job of fitting the tabulated values of ref. 18 for I_r's of chemical interest. The largest error is in determining the barrier height V and the rotational "degeneracy" for non-symmetrical functional groups.

Error estimates. There are two major sources of uncertainty in the calculated heats of formation: 1) uncertainties resulting from the applicability of the theoretical methods to a given molecule and 2) systematic uncertainties resulting from lack of good reference compounds for the BACs. The magnitude of the first is estimated using an *ad hoc* method developed previously that uses the results from lower-level calculations[2] and is provided on the web site for each molecule in the data base:

$$Error(\text{BAC-MP4}) = \{1.0 \text{ kcal mol}^{-1} + (\Delta H_{\text{BAC-MP4}} - \Delta H_{\text{BAC-MP3}})^2 + (\Delta H_{\text{BAC-MP4}} - \Delta H_{\text{BAC-MP4SDQ}})^2 + 0.25(E_{\text{BAC}}(\text{spin}_{S^2}) \text{ or } E_{\text{BAC}}(\text{spin}_{\text{UHF-I}}))^2\}^{1/2} \quad (17)$$

The second source of uncertainty can add a few kcal mol^{-1} to the uncertainty estimates and will scale with the number of bonds in the molecule. The use of different reference values would shift our calculated heats of formation as a group, with the consequence that calculated bond dissociation enthalpies and reaction enthalpies are affected less than the heats of formation. Overall, we believe that the uncertainties in the BAC-MP4 heats of formation lie in the ± 2-7 kcal mol^{-1} range.

The BAC-G2 Method

Overview of the BAC-G2 method. The BAC-G2 method[4] applies the BAC corrections to the standard G2 method,[19] using the Gaussian quantum-chemistry codes. The electronic-structure calculations to determine the geometry, vibrational frequencies, and electronic energies are the same as those in the G2 method. Specifically, the geometry and vibrational frequencies in the BAC-G2 method are obtained from a Hartree-Fock (HF) calculation (restricted Hartree-Fock, RHF, for closed shell molecules and unrestricted Hartree-Fock, UHF, for open shell molecules) using the 6-31G(d) split-valence basis set with polarization functions on the heavy (non-hydrogen) atoms. At this level of theory, vibrational frequencies are systematically too large compared to experimental values. We therefore scale the HF harmonic frequencies downward by 12 percent. The electronic energies at the QCI, MP4, and MP2 levels of theory, as well as the collective G1, G2MP2, and G2 electronic energies, are taken directly from the output of the G2 method. The basis sets are the same as those defined in the standard G2 method. The geometry used in the single-point calculations is obtained by reoptimizing the HF geometry at the MP2 level, again as defined in the G2 method.

BAC corrections. The BAC corrections for the BAC-G2 method are those defined previously.[4] Briefly, three types of corrections ($E_{\text{BAC-}}$; units of energy) are used: atomic, molecular, and bondwise, indicated in Equations (18)—(21) below. The atomic correction depends on the atom type:

$$E_{\text{BAC-atom}} = \sum_k E_{\text{BAC-atom}}(A_k) \quad (18)$$

where the sum runs over all the atoms in the molecule. The value of $E_{\text{BAC-atom}}$ (A_k) depends on the atom type and A_k is an adjustable parameter.

The molecular BAC correction arises from errors in the overall electronic structure of the molecule. The BAC correction for this term is given by

$$E_{\text{BAC-molecule}} = E_{\text{BAC-elec pair}} \tag{19}$$

where $E_{\text{BAC-elec pair}}$ depends on the difference between the spin of the molecule and the sum of the spins of the constituent atoms:

$$E_{\text{BAC-elec pair}} = K_{\text{elec pair}}(\text{Spin}_{\text{molecule}} - \sum_{atom} \text{Spin}_{\text{atom}}) \tag{20}$$

where $K_{\text{Elec pair}}$ is an empirically adjusted parameter for a given BAC method and "Spin" refers to the S quantum number.

The third type of BAC correction depends on the formation of chemical bonds. In this instance, we distinguish between bonds and pair-wise interactions. A bond is taken to mean the formation of an electron pair between the atoms. This correction addresses systematic errors arising from electron-pairing not covered by Eqn. 20. The correction for each bond A-B in the molecule having neighbors C and D (e.g., C-A-B-D) is given by

$$E_{\text{BAC-bond}}(AB) = A_{AB} e^{-\alpha R_{AB}} + \sum_{C} B_{CA} + \sum_{D} B_{DB}, \tag{21}$$

where the first term is the correction for the bond alone, while the corrections for its nearest neighbors are treated as a sum of corrections for each neighbor of the form

$$B_{CA} = B_C + B_A. \tag{22}$$

The B_A's are constants that depend only on the type of atom. The bond-distance dependence in Eqn. 21 exists only in the first term for the bond itself. Furthermore, α no longer depends on the type of bond, as it did in the original BAC method.[3] Note that the bond-wise corrections do not go to zero at infinity, due to the terms $\Sigma B_{CA} + \Sigma B_{DB}$ defined by Eqn. 22.

The parameters for each of the corrections are given in Table 3; values of all parameters with the exception of those for aluminum (see below) were determined previously.[4] The atomic corrections (Eqn. 18) are straightforward. For the bond-wise corrections (Eqn. 21), the α exponent is taken to be 3.0 $Å^{-1}$, while the pre-exponential coefficient A_{AB} is taken to be the geometric mean of the individual atom types, i.e.,

$$A_{AB} = -(A_{AA} A_{BB})^{1/2}. \tag{23}$$

Equation 21 also includes contributions from the nearest-neighbor B_{ij} terms (defined by Equation 22). The accuracy of the parameters comprising these terms (see Table 3) is difficult to assess because of their small size. This is due to the fact that to date we have only applied the BAC-G2 method to relatively small molecules (less than seven heavy, i.e., non-hydrogen, atoms), for which accurate experimental thermodynamic data exist. However, these terms become quite significant for larger molecules and for halides (see below). Unfortunately, given the limited

accuracy of experimental data for larger non-hydrocarbon, unsaturated gas-phase species it will remain difficult to establish the accuracy of the B_{atom} terms.

Table 3. BAC-G2 Parameters (Energies in kcal-mol^{-1}) and atomic heats of formation used in the calculations of heats of formation.

$K_{Elec\ pair}$ = 0.860				ΔH_{f0}^{o} [a]
Atom	A_{Atom}	B_{Atom}	A_{ii}	
H	0.485	-0.146	1.462	51.15
C	1.081	0.051	0.0	168.90
N	1.498	-0.010	2.281	111.03
O	-0.501	-0.010	114.3	59.49
F	-1.942	0.215	373.1	20.41
Al	-1.500	0.000	300.0	79.73
Si	0.097	0.008	297.4	106.56
Cl	-0.776	0.087	1433.7	29.37

[a] Atomic heat of formation at 0 K, kcal mol^{-1}, obtained from the BAC-G2 method.

Heats of formation. The corrected heat of formation at 0 K (ΔH_{f0}^{o}) can now be obtained from the calculated electronic energy. First, the electronic energy is added to the zero-point energy (which is automatically included in the G2(0 K) output of the Gaussian-94 and Gaussian 98 codes). Next, the resulting energy is subtracted from the electronic energies of the atoms to give an electronic heat of atomization:

$$E_{\text{atomization}} = \sum_{i}^{n} E_i\,(\text{atoms}) - (E_{\text{ab initio}}\,(\text{molecule}) + E_{\text{ZPE}}) \tag{24}$$

Referencing this energy against the BAC-G2 ΔH_{f0}^{o} at 0 K of the atoms (given in Table 3) in the gas phase yields the uncorrected ΔH_{f0}^{o}:

$$\Delta H^{\circ}_{\text{f0, uncorrected}} = \sum_{\text{atoms}} \Delta H^{\circ}_{\text{f0, atoms}} - E_{\text{atomization}} \tag{25}$$

Subtracting the BAC corrections from this energy finally yields ΔH_{f0}^{o} at 0 K:

$$\Delta H^{\circ}_{\text{f0, BAC}} = \Delta H^{\circ}_{\text{f0, uncorrected}} - E_{\text{BAC-Correction}} \tag{26}$$

Thermodynamic data as a function of temperature. Heats of formation, entropies, and free energies at various temperatures are then obtained using equations derived from statistical

mechanics (the same procedure as in the original BAC-MP4 method, which includes corrections for hindered rotors, such as CH_3 groups; see discussion above). Thus, for finite temperatures, the raw G2 energies (without BAC corrections) obtained from the BAC-G2 method do not correspond to those from the output of a Gaussian G2 calculation, since hindered rotors are included in the BAC procedure.

Error estimates. Using an *ad hoc* expression similar to that formulated for the earlier BAC-MP4 method[2] we obtain an estimate of the error (or confidence level) in the BAC-G2 method. In this case, we use the similarities between the G1 and G2-MP2 methods and the G2 method itself as an indication of the error:

$$\text{Error (BAC-G2)} = \text{Sqrt}\ \{\ 1.0\ \text{kcal-mol}^{-1} + (\Delta H_{\text{BAC-G2}} - \Delta H_{\text{BAC-G2MP2}})^2 + (\Delta H_{\text{BAC-G2}} - \Delta H_{\text{BAC-G1}})^2\}. \quad (27)$$

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